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FORMATION OF FILM ON A METAL SURFACE
[Kinzoku hyomen no himaku keisei houhoh]

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Claim

A method for formation of a film on a metal surface characterized by coating an aqueous solution or an alcohol mixed aqueous solution containing one or more different types of organic silicon monomers having at least two different reactive groups in the molecule and one or more different types of compounds selected from among the group consisting of fluorine compounds of titanium and/or zirconium onto the surface of a metal followed by drying.

Detailed explanation of the invention

The present invention pertains to a surface treatment method consisting of coating an aqueous solution or an alcohol mixed aqueous solution containing an organic silicon monomer having at least two different reactive groups in the molecule, that is, a silane coupling agent and a fluorine compound of titanium and/or zirconium onto the surface of the metal and drying the film to provide a surface treatment method for forming a film having excellent corrosion resistance and adhesiveness to paint.

In the past, as a means to improve corrosion resistance for metals and adhesiveness with paint, the chromate treatment method, phosphate treatment method, etc., have been commonly used. The chromate treatment method is accompanied by disadvantages such as a reduction in the adhesivity with paint with the passage of time, furthermore it is accompanied by difficulties in terms of waste water treatment due to chromic acid pollution regulations, and furthermore, there is the additional fact that it becomes a hazardous secondary pollution generating source due to elution of chromic acid from the film formed. On the other hand, in general, a film treatment with zinc phosphate, iron phosphate, etc., is provided, but the zinc phosphate is a crystalline film and when used as a undercoating for paint, problems such as destruction of the crystalline film during the course of a folding process exists. In comparison to zinc phosphate based film, the thickness of the film is thinner and the corrosion resistance is inferior for iron

phosphate-based films; thus, a post treatment such as a treatment with a chromate is commonly provided.

The purpose of the present invention is to eliminate the aforementioned problems and to develop a pollution-free surface treatment process, and furthermore, to provide a surface treatment method with excellent corrosion resistance and adhesiveness with paint suitable for surface preparation at the time of coating, etc., using a dry coat system advantageous for waste water treatment, etc.

As a result of much research conducted by the inventors of the present application on pollution-free surface treatment methods with an absence of the aforementioned existing problems, they discovered that formation of a film having excellent corrosion resistance and adhesivity with paint could be achieved when coating was first done for a metal surface with an aqueous solution or an alcohol mixed aqueous solution containing one or more different types of organic silicon monomers having at least two different reactive groups in the molecule (hereinafter referred to as silane coupling agent) and one or more different types of compounds selected from the group consisting of fluorine compounds of titanium and/or zirconium onto the surface of the metal, and then drying to form the coated material without providing a water wash, and as a result, the present invention was accomplished.

The silane coupling agent used as one of components in the present invention has a function of chemical bonding organic materials and inorganic materials and has been widely used as an adhesive for industrial products, and when a silane coupling agent is coated onto the surface of a metal and used as a surface treatment film for metals, adhesivity of films such as paint, polymer resins, etc., to the metal is increased and the effect of the treatment can be recognized. However, a sufficient increase in corrosion resistance on the surface of the metal, which is the primary purpose of the surface treatment of metals, is absent and the aforementioned material is accompanied by problems when used as a practical surface treatment film for metals. Furthermore, for examples of prior art where a silane coupling agent is used as

a component of a surface treatment agent for metals, those disclosed in Japanese Kokai Patent Application No. Sho 51[1976]-63328, Japanese Kokai Patent Application No. Sho 51[1976]-119338, Japanese Kokai Patent Application No. Sho 52[1977]-130444, Japanese Kokoku Patent Application No. Sho 55[1982]-41711, Japanese Kokoku Patent Application No. Sho 55[1982]-41713, Japanese Kokoku Patent Application No. Sho 55[1987]-41712, etc., can be mentioned, and the metal surface treatment solution used in the aforementioned inventions are water-soluble or water-dispersed polymer resins mixed with phosphate, silica and oxides of titanium, zirconium, molybdenum, etc., or a treatment solution containing an organic compound mixed with a silane coupling agent. On the other hand, as a result of much research conducted by the inventors of the present application in an effort to increase the adhesivity with paint and increase the corrosion resistance and improve the coating, the inventors discovered that formation of a film having excellent adhesivity with paint and corrosion resistance could be made possible without using a composition comprised of a water-soluble or water-dispersible polymer resin, phosphate, silica, etc., when a composition formed by adding a fluorine compound of a water-soluble titanium and/or a zirconium to an aqueous solution or alcohol solution of silane coupling agent to mix and the aforementioned composition was coated onto a metal surface and drying the film. The surface treatment solution of the present invention is very stable; thus, formation of deposits of each component used in the composition is absent when the aforementioned treatment solution is used in practice, furthermore, a continuous treatment of the metal surface can be safely achieved on an industrial scale, and furthermore, efficient formation of a film having excellent adhesivity with paint and corrosion resistance is made possible. It is not well understood why the significant increase in corrosion resistance is achieved as a result of adding a fluorine compound of titanium and/or zirconium, but it is hypothesized that a composite film having high physical and chemical stability is formed as a result of bonding between the silane coupling agent component and the fluorine compound of titanium and/or

zirconium during the course of the film formation process at the time of coating and drying of the composition of the present invention on the metal or during the film formation process for the paint, polymer resin, etc., that follows. And furthermore, it is known that in comparison to phosphoric acid ions or phosphate, a higher solubility and activation of the passive state film on the surface of the metal can be achieved when a fluorine ion or fluorine compound is used, and it is hypothesized that the fluorine ion or fluorine compound included in the treatment solution of the present invention undergoes a reaction with the metal surface during the film formation process at the time of coating and drying; as a result, an increase in bonding between the metal and the film is made possible.

A different purpose of the present invention is to achieve high corrosion resistance and adhesivity with the paint through a surface treatment for paints and polymer resins with a very thinly coated film at a ratio of approximately 10-300 mg/m^2, and the aforementioned purpose is achieved by the present invention, as well.

The inventors of the present application discovered that formation of a film having excellent corrosion resistance and adhesivity with the paint on the surface could be achieved when a noble metal surface treatment solution that does not belong to the prior art, that is, a metal surface treatment solution having a composition comprised of a silane coupling agent and a fluorine compound of titanium and/or zirconium is coated onto the metal surface and dried, and as a result, the present invention was accomplished.

"The organic silicon monomers having at least two different reactive groups in the molecule," that is, the silane coupling agent, used in the present invention is an organic silicon monomer having a reactive group that undergoes reaction with an inorganic substance (methoxy group, ethoxy group, silanol, etc.) and a reactive group that undergoes reaction with an organic substance (vinyl group, epoxy group, methacrylic group, amino group, etc.) in the molecule, and for the aforementioned compounds,

trimethylmethoxy silane, γ-amino propyl triethoxy silane, γ-amino propyl trimethoxy silane, N-β-(aminoethyl) γ-amino propyl trimethoxy silane, N-β-(aminoethyl) γ-amino propyl methyl diethoxy silane, vinyl triethoxy silane, vinyl tris(β-methoxy ethoxy) silane, divinyl dimethoxy silane, γ-glycidoxy propyl trimethoxy silane, γ-methacryloxy propyl trimethoxy silane, etc., can be mentioned. For examples of fluorine compounds of titanium and zirconium, titanium fluoride hydracid, ammonotitanium fluoride, zirconium fluoride hydracid, ammonozirconium fluoride, etc., can be mentioned, and furthermore, a reaction can be conducted for a metal, an oxide, an hydroxide, or an ammonium carbonate of titanium and/or zirconium with a fluoroacid, which is dissolved to form a fluorine compound of titanium or zirconium, and used.

The concentration of the silane coupling agent used in the present invention is in the range of 0.5-100 g/L, preferably, in the range of 1-50 g/L. When the concentration is 0.5 g/L or less, the effect of the silane coupling agent cannot be observed; on the other hand, when the concentration is 100 g/L or more, a further increase in the effect of the silane coupling agent cannot be expected and is wasteful. Meanwhile, the concentration of the second component, that is, the fluorine compound of titanium and/or zirconium, is in the range of 0.01-5 g/L, preferably, in the range of 0.05-1.0 g/L in the form of titanium or zirconium. When the concentration is 0.01 g/L or less, the effect of the fluorine compounds of titanium and/or zirconium cannot be observed; on the other hand, it is wasteful when 5 g/L or more is used. In this case, the ratio of the silane coupling agent and the fluorine compounds of titanium and/or zirconium is in the range of 10-200:1 (titanium or zirconium converted score), and preferably, in the range of 20-100:1.

As a solubilizer or stabilizer of the chemical components in the silane coupling agent in an aqueous medium, alcohols such as methanol, ethanol and propanol may be added to the surface treatment solution of the present invention as needed.

For the treatment object used in an embodiment of the present invention, in addition to standard metals, for example, copper, copper alloys, aluminum and aluminum alloys, zinc and zinc alloys, zinc plating and zinc plated steel and tin plating and tin plated steels, standard zinc phosphate or iron phosphate treated steel, zinc phosphate treated lead plated steel, phosphate treated tin plated steel, chromate treated zinc plated steel, etc., can be mentioned. The method for film formation of the present invention is used to achieve a direct surface treatment effect for metals of the former; in other words, the method is used to provide a film having excellent corrosion resistance and adhesivity with paints on the surface of a metal, and to achieve a further effect for the phosphate-treated plated steel, chromate-treated zinc-plated steel, etc., of the latter, that is, to provide a further increase in the corrosion resistance and adhesivity with the paint film.

For coating of the surface treatment solution of the present invention, known materials, for example, brush coating, spray coating, roll coating, dip coating, etc., can be used without any restriction.

For drying of the aforementioned surface treatment solution of the present invention after coating, standard drying methods may be used in this case and for the drying temperature, a temperature in the range of 60-300°C can be freely selected.

Working examples of the present invention are described below.

Working Example 1

Composition of the treatment solution

10 g of vinyl triethoxy silane (Product of Shinetsu Chemical Co. Ltd., Trade name KBE1003)

100 g of methanol

1 g of ammonotitanium fluoride

Water was added to make 1 L. The pH in this case was 4.0.

After cleaning a steel sheet, a zinc plated steel sheet, and an aluminum sheet with a 1% hot aqueous solution of an alkali degreasing agent (Registered trademark, Parco-Cleaner 364 S [transliteration], Product of Nippon Parkerizing Co. Ltd.), the aforementioned sheets were dipped in the aforementioned treatment solution for 5 sec and squeezed with rolls and drying was done for 30 sec with hot air heated to 120°C. For the treatment objects obtained as described above, an acrylic based paint was coated to form a thickness of 20-25 μm, baking was carried out for 3 min at 200°C and when a test was carried out for the aforementioned coated sheets, those treated with the treatment solution of the present invention showed excellent test results in corrosion resistance and adhesivity with paint as shown in Table 1 below.

Working Examples 2-4

Using the treatment compositions of Working Examples 2-4 shown below, a treatment was carried out for the steel sheet, zinc-plated steel sheet, and aluminum sheet under the conditions described in Working Example 1, and furthermore, coating was done under the conditions described in Working Example 1, and a test was conducted for the coated sheets obtained.

Composition of the treatment solution of Working Example 2

5 g of Methacryl oxypropyl trimethoxy silane (Product of Shinetsu Chemical Co. Ltd., trade name: KBM503)

20 g of ethanol

0.2 g of zirconium fluoride hydracid

0.2 g of titanium fluoride hydracid

Water was added to make 1 L. The pH in this case was 3.0.

Composition of the treatment solution of Working Example 3

30 g of N-β-(aminoethyl) γ-amino propyl trimethoxy silane (Product of Shinetsu Chemical Co. Ltd., trade name: KBM603)

3 g of ammonotitanium fluoride

Water was added to make 1 L. The pH in this case was 11.0.

Composition of the treatment solution of Working Example 4

10 g of γ-aminopropyl triethoxy silane (Product of Shinetsu Chemical Co. Ltd., trade name: KBM903)

1 g of zirconium fluoride hydracid

Water was added to make 1 L. The pH in this case was 10.0.

The corrosion resistance and the adhesivity with paint of the treatment objects treated with the treatment solutions of the aforementioned Working Examples 2-4 exhibited excellent test results.

Comparative Examples 1-4

Using the compositions of the treatment solution of Comparative Examples 1-4 shown below, a treatment was conducted for a steel sheet, a zinc-plated steel sheet, and an aluminum sheet under the conditions described in Working Example 1, and furthermore, coating was done under the conditions described in Working Example 1, and a test was conducted for the coated sheets obtained.

Composition of treatment solution of Comparative Example 1

(The composition of treatment solution of Working Example 1 without ammonotitanium fluoride)

10 g of vinyl triethoxy silane

100 g of methanol

Water was added to make 1 L. The pH in this case was 4.0.

Composition of treatment solution of Comparative Example 2

(The composition of treatment solution of Working Example 2 without zirconium fluoride hydracid and titanium fluoride hydracid)

5 g of methacryloxy propyl trimethoxy silane

20 g of ethanol

Water was added to make 1 L. The pH in this case was 3.5.

Composition of treatment solution of Comparative Example 3

(The composition of treatment solution of Working Example 3 without ammonotitanium fluoride)

30 g of N-β-(aminoethyl) γ-amino propyl trimethoxy silane

Water was added to make 1 L. The pH in this case was 11.0.

Composition of the treatment solution of Comparative Example 4

(The composition of treatment solution of Working Example 4 without zirconium fluoride hydracid)

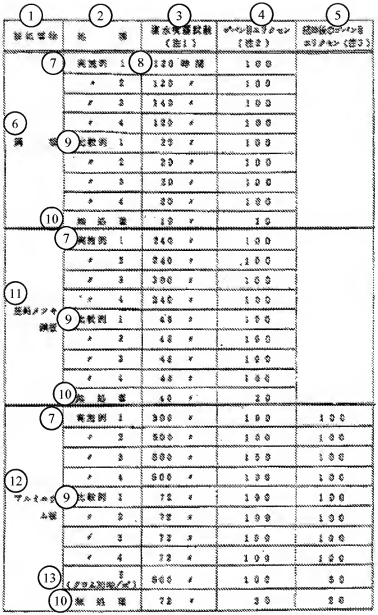
10 g of γ-aminopropyl triethoxy silane

Water was added to make 1 L. The pH in this case was 10.5.

Comparative Example 5

After cleaning an aluminum sheet with a 1% hot aqueous solution of an alkali degreasing agent (aforementioned Parco-Cleaner 364 S [transliteration]), a chemical treatment was provided with a 7% hot solution used for chromate treatment (Registered trademark, Bondelite 713 [transliteration]) and water wash was further provided and coating was provided under the conditions described in Working Example 1 and a test was conducted the aforementioned coated sheet obtained.

TABLE 1



1	2	3	4	5
被処理物	処　理	塩水噴霧試験（注1）	エリクセン（注2）	経時後のエリクセン（注3）
7	実施例 1	120 時間	100	
	〃 2	125 〃	100	
	〃 3	140 〃	100	
6	〃 4	125 〃	100	
鋼板	9 比較例 1	25 〃	100	
	〃 2	20 〃	100	
	〃 3	30 〃	100	
	〃 4	20 〃	100	
10	無処理	10 〃	10	
7	実施例 1	240 〃	100	
	〃 2	240 〃	100	
	〃 3	300 〃	100	
11	〃 4	240 〃	100	
亜鉛メッキ	9 比較例 1	48 〃	100	
鋼板	〃 2	48 〃	100	
	〃 3	48 〃	100	
	〃 4	48 〃	100	
10	無処理	48 〃	20	
7	実施例 1	500 〃	100	100
	〃 2	500 〃	100	100
	〃 3	500 〃	100	100
12	〃 4	500 〃	100	100
アルミニウム	9 比較例 1	72 〃	100	100
板	〃 2	72 〃	100	100
	〃 3	72 〃	100	100
	〃 4	72 〃	100	100
13	3 （クロム酸処理）	500 〃	100	50
10	無処理	72 〃	20	20

Key 1 Treatment object

2 Treatment

3 Salt water spray test (Note 1)

4 Erichsen cross-cut adhesion test (Note 2)

5 Erichsen cross-cut adhesion test with time (Note 3)

6 Steel sheet

7 Working Example

8 Hours

9 Comparative Example

10 Without treatment

11 Zinc plated steel sheet

12 Aluminum sheet

13 (chromium 30 mg/m^2)

(Note 1) Salt water spray test

According to the specification of the JIS Z-2317, the time required for swelling at the cross cut area of the coated film was used.

(Note 2) Erichsen cross-cut adhesion test

According to the test method specified in "The Paint Test Method" by the Paint Industry of Japan, 100 cross-cuts measuring 1 mm^2 were formed on the coated film, the back side of the coated surface provided with the cross cuts was pressed by 3 mm using the Erichsen Tester and an adhesive tape was applied to the coated surface of the projecting area. Subsequently, the tape was peeled from the coated surface and the number of squares which were not peeled from the coated film with the cross-cut were counted.

(Note 3) Erichsen cross-cut adhesion test with time

The treatment object was stored at 40°C for 7 days and coating is provided and the test described in the aforementioned (Note 2) is conducted on the coated sheet.